Long-term trends (1975–2014) in the concentrations and export of carbon from Finnish rivers to the Baltic Sea: organic and inorganic components compared.

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Abstract:	Finnish rivers exported annually on average 1.2 M t carbon, and total organic carbon (TOC) comprised the major share (nearly 80%) of this export. The mean area specific carbon export was 4.5 g C m-2 yr-1. The highest organic carbon export originated from peat dominated catchments, whereas rivers draining agricultural catchments had the highest area-specific inorganic carbon fluxes. Between 1975 and 2014 total inorganic carbon (TIC) concentrations rose more steadily than the respective TOC concentrations. There was an overall decrease in TOC concentrations between 1975 and the mid-1990s. Decreased point source loading contributed to this pattern, although decreases were also detected in rivers without any major pollution sources. From the mid-1990s TOC concentrations started to rise and the increase was even more pronounced than the earlier decrease. The upward trend was ubiquitous, both in time and space, and it was not possible to link the changes to any specific catchment characteristics or another single driver. Warming climate, changes in hydrology and decreases in acidic deposition were the major driving factors although their contribution varied geographically. At the same time both TOC and TIC export increased slightly, but the strong upward trends in TOC concentrations were not reflected in TOC export trends. This was because changes in hydrographic flow had a dominant influence on TOC export to the sea and any changes in concentrations were masked behind the variation in flow.
Response to Reviewers:	Reply: Page 2, Line 48: Add ‘the’ before ‘USA’ Done Page 4, 3rd line: Delete the first ‘was’ in ‘median was r2 was 0.92’. Also just to clarify, did you use a single TIC-alkalinity regression equation for all sites? Done

Page 5, line 43: Change ‘locating’ to ‘located’.
Done
Page 8, line 39: Change ‘atmospheric’ to ‘atmosphere’
Done
Page 10: It seems possible that your explanation for decreasing DOC from 1975-1994 (decreasing point source pollution) could also have contributed to a delayed increase in DOC in response to declining acid deposition? If the decrease in point source pollution was continuing through the 1980s then this would have reduced one component of the total DOC (pollution), so that even if another component (natural DOC) was increasing in response to decreasing acid deposition, you would not yet observe this in the total DOC trends because the two changes would cancel out. Then when the point source pollution inputs stabilised, DOC would begin to increase. This is just an idea, which you are welcome to disagree with! I am certainly not insisting that you revise the paper to incorporate it, just thinking about a possible explanation for the timing of your trends. To me, the ubiquity of the trends does point towards a single driver.

Reply: We still think that acidic deposition is partly behind the increases, but that also other factors (related to climate and hydrology) affect the trends.

Page 11, 2nd line: It might help to clarify here that this sentence refers to years with mild winters?
Done
Page 11, line 7: Add ‘the’ before ‘early 1990s’.
Done
Page 11, line 51: ‘Uphill’ should be ‘upland’
Done
Page 12, line 1: Add a ‘to’ to ‘we wanted study’.
Done
Page 12, line 15: Add ‘the’ before ‘positive trend’. In relation to this interpretation, see my comments above – if the underlying trend in catchment-derived DOC since the 1970s was upward (but masked by a downward trend in point-source pollution DOC) then perhaps your hypothesis about DOC mineralisation generating DIC would still be plausible? That assumes that the point source pollution component is not being processed in lakes in the same way as the natural DOC (or that the point sources are downstream of the lakes) which may or may not be correct.
Reply: we have slightly modified the text accordingly.
Page 12, line 23: I’d suggest that the heading should be “Why are trends in TOC export and concentrations not similar?”
Done
Page 12, line 36: Delete 2nd ‘years’.
Done
Page 12, line 48: Add ‘an’ before ‘upward’.
Done
Page 13, line 39: Change ‘Instead of single driver’ to ‘Instead of a single driver,’
Done
Page 13, lines 41-16: It may indeed be tempting to link the increase in TOC to climate change, but I am not so sure that the evidence presented in the paper supports this! Rather than introducing what is effectively a new hypothesis in the conclusions, I think it would be better to focus on the implications of the very clear trends you have observed.
Reply: We still think it is part of the story.

Also, on the subject of rising C concentrations in Finnish coastal waters, I think it may be more relevant that the DOC and DIC concentrations in rivers have increased (a lot) rather than that the changes in export appear smaller. As I understand it the water in the Baltic is largely comprised of freshwater coming from the surrounding countries, in which case surely it will be the concentration of solutes in that water which determine the concentration of these solutes in the sea, not the fluxes? This is a bit different to a well-mixed ocean, where most of the water does not come directly from the rivers, and so the solute fluxes in river inputs will (I think) be more important than the concentrations.
Reply: In this respect we disagree: the export (the amount of carbon) is more

	important, because it controls the concentration of TOC in Finnish coastal waters. TOC concentration in river water may be extremely high during low flow events without any major impact in sea water.

Long-term trends (1975 – 2014) in the concentrations and export of carbon from Finnish rivers to the Baltic Sea: Organic and inorganic components compared.

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Keywords: organic carbon, inorganic carbon, concentration, riverine export, long-term trends, Baltic Sea

Abstract

Finnish rivers exported annually on average 1.2 M t carbon, and total organic carbon (TOC) comprised the major share (nearly 80%) of this export. The mean area specific carbon export was 4.5 g C m^{-2} yr^{-1}. The highest organic carbon export originated from peat dominated catchments, whereas rivers draining agricultural catchments had the highest area-specific inorganic carbon fluxes. Between 1975 and 2014 total inorganic carbon (TIC) concentrations rose more steadily than the respective TOC concentrations. There was an overall decrease in TOC concentrations between 1975 and the mid-1990s. Decreased point source loading contributed to this pattern, although decreases were also detected in rivers without any major pollution sources. From the mid-1990s TOC concentrations started to rise and the increase was even more pronounced than the earlier decrease. The upward trend was ubiquitous, both in time and space, and it was not possible to link the changes to any specific catchment characteristics or another single driver. Warming climate, changes in hydrology and decreases in acidic deposition were the major driving factors although their contribution varied geographically. At the same time both TOC and TIC export increased slightly, but the strong upward trends in TOC concentrations were not reflected in TOC export trends. This was because changes in ~~hydrographic~~ flow had a dominant influence on TOC export to the sea and any changes in concentrations were masked behind the variation in flow.

1. Introduction

The Baltic Sea and its surrounding catchments are facing multiple major environmental changes that greatly impact ~~on the~~ ecosystems, and which are in turn tightly linked to ~~the large-scale carbon cycle:~~ Climate change (Denman et al., 2007), eutrophication (HELCOM, 2009) and acidification (Omstedt et al., 2012). These phenomena interact in a complex manner both on land (Settele et al., 2014), in aquatic ecosystems (Cole et al., 2007; Cai et al., 2011; Battin et al., 2009) and at the complex interfaces between the two (Fleming-Lehtinen et al., 2015; Asmala et al., 2013, 2014). Organic and inorganic forms of carbon have different implications for the biogeochemical carbon dynamics of the receiving water bodies (Cole et al., 2007): Organic carbon (OC) export may strengthen the effects of eutrophication in marine waters due to the mineralization of organic matter, which will result in enhanced oxygen demand, production of CO_2 and thus also acidification (Cai et al., 2011; Jutterström et al., 2014). On the other hand coloured organic matter absorbs photosynthetically active radiation, which can result in decreasing primary production (Thrane et al., 2014). Dissolved inorganic carbon (DIC) export may mitigate acidification effects (Aufdenkampe et al., 2011) since the inorganic carbon (IC) transported by rivers is an important source of marine alkalinity (Sundqvist, 1993). Moreover, acidification can be partly counteracted in anoxic bottom waters by increased alkalinity (Edman and Omstedt, 2013).

The major components of both the OC and IC pools, especially in coastal waters of the Baltic Sea, originates in the catchment area and is transported to the sea by rivers (Alling et al., 2008; Humborg et al., 2010; Räike et al., 2012; Fleming-Lehtinen et al., 2015). OC exported to the sea is mainly of terrestrial origin, and in Finland peat soils are a major source of OC (e.g. Mattsson et al., 2005; Asmala et al., 2014; Hoikkala et al., 2015). The sources of IC are more variable and include weathering of carbonate and silicate minerals, mineralisation of organic matter (both in terrestrial and aquatic ecosystems), soil respiration and groundwater inputs (Meybeck et al., 1993; Raymond and Cole, 2003).

The total global carbon (TC) flux from the continents to the oceans is 0.9 G t C yr^{-1}, approximately in equal proportions of IC and OC (Cole et al., 2007). The geographical variation between the different forms is globally large e.g. DIC dominates in rivers draining the conterminous United States and in many Arctic rivers (Striegl et al., 2007; Tank et al., 2012; Guo et al., 2012), whereas dissolved organic carbon (DOC) dominates in boreal rivers and lakes draining peat dominated catchments (Rantakari and Kortelainen, 2008; Humborg et al., 2010; de Wit et al., 2015). Finnish rivers export on average around 0.9 M t total organic carbon (TOC) annually into the Baltic Sea (Räike et al., 2012). However, the corresponding amount of total inorganic carbon (TIC) export has been less studied and the TC (TC = TOC + TIC) ~~export into~~ the Baltic Sea from Finnish rivers has not been reported.

Organic carbon concentrations have increased in many freshwaters of the northern hemisphere (Evans et al., 2005; Monteith et al., 2007; de Wit et al., 2007; Clark et al., 2010) and also in northern Baltic Sea coastal waters (Fleming-Lehtinen et al., 2014). In contrast, there is no clear indication that DOC export to the Baltic Sea from Finnish rivers has increased since 1975, although there is evidence that the projected mild winters in the future will most likely lead to increased DOC export (Räike et al., 2012; Lepistö et al, 2015; Mattsson et al., 2015). Studies in the USA have shown an increase in DIC export to the oceans (Stets et al., 2014) and most notably DIC export from the Mississippi River has been increasing over the last 50 years (Raymond and Cole, 2003). In the Baltic Sea region an increasing trend in alkalinity has been measured in rivers draining to the Gulf of Finland over the last 100 years, whereas a decreasing trend was detected in rivers entering the Gulf of Bothnia (Hjalmarsson et al., 2008). Otherwise, trends in riverine TIC export to the Baltic Sea are largely unknown and it is pertinent to question whether or not increasing alkalinity export in a warming climate is also happening in high latitude rivers, such as those draining into the northern basins of the Baltic Sea (Smith et al., 2008)~~?~~

The aim of this study was to estimate carbon (TIC and TOC) export to the Baltic Sea from Finnish rivers and to investigate trends in the export and concentrations between 1975 and 2014. By combining the results of these two carbon fractions we were able to calculate TC export to the Baltic Sea from Finnish rivers and to estimate the changes in the export over time. To separate the effects of hydrological changes from other factors we estimated both flow normalised and non-normalised fluxes. We compared TIC and TOC export and changes in the export in relation to catchment properties and investigated if there was a discrepancy between trends in carbon concentrations and export, and the possible reasons for any differences.

2. Materials and methods

The study was based on the long-term monitoring results of 29 Finnish rivers discharging into the Baltic Sea. The total catchment area of the studied rivers was nearly 275,000 km^2, which covers 91% of the Finnish Baltic Sea catchment area and includes highly variable hydrological and geological features, land-use patterns and population density. The areas of the 29 river basins range from 357 to 61,466 km^2. For each basin, the different land use classes were derived from satellite image-based land-cover and forest classification data (CORINE Land Cover 2006: 25×25 m grids).The proportion of upland forests ranges from 33 to 54% (average 47%) and the proportion of peatlands from 3 to 40% (average 18%). The percentage of peat is highest at latitudes between 63° and 66° N, ~~whereas forests increase~~ towards the south. The mean proportion of agricultural land in the river basins was ~~on average~~ 7% (range 1 to 43%), and the majority of this is located close to the southern and western coasts. The water area of the catchments ranges from 0.5 to 19% (average 10%). Urban areas 3% (range 1 to 20%) are concentrated in southern Finland. The mean annual flow of all rivers varied from 4 to 622 m^3s^{-1}, and annual runoff from 201 to 459 mm (Table 1). Runoff is usually higher in northern parts of the country where evaporation is lower. Spring peak-flow normally occurs in April in southern and central parts of the country and in May in northern regions. More detailed information of the location of sampling stations and basic catchment characteristics can be found in Räike et al. (2012).

Data on water quality and water flow from 1975 to 2014 were derived from national databases maintained by the Finnish Environment Institute (SYKE). Water quality data were derived from the Finnish National Monitoring Programme of riverine inputs into the Baltic Sea. The sampling depth was 1 m. The total number of analyses used was: 4,400 TIC, 14,500 alkalinity and 13,000 TOC analyses. The median annual sampling frequency was 12 (varied from 5 to 20 in individual rivers). The total number of annual alkalinity analyses varied during the study period, reaching a maximum in the late 1990s (nearly 500 analyses per year), whereas in 1981 only 143 alkalinity samples were analysed. The number of annual TIC analyses varied between 243 and 367.

TIC analyses were first included in the Finnish Monitoring Programme of River Water Quality in 2003, and in order to reconstruct a time-series back to 1975 TIC concentrations were estimated from the measured alkalinity values using the regression equation TIC [mg L^{-1}] = 11.8 * Alkalinity [mmol L^{-1}] + 0.52, r^2 = 0.95, n = 4436, based on simultaneous TIC and alkalinity measurements (Fig. 1). In most of the rivers the correlation between TIC and alkalinity was good (median r^2 was 0.92; Table 1). The weakest correlation (r^2 = 0.48) was detected in a river in northern Finland (the Oulujoki river, Basin No. 59) loaded both by diffuse and point source pollution. We also reconstructed our time series with river-wise regression equations, but the difference was negligible. Reconstructed data were used only in trend analyses.

The acidified TOC samples were bubbled with nitrogen to remove inorganic carbon (CO_2) and TOC was analysed from unfiltered samples by oxidation to CO_2 followed by IR-measurements. Samples for TIC were put into airtight bottles and placed in coolers while in transit to the laboratory. TIC was measured in the laboratory using infrared spectroscopy. The Gran method (obtained using pH 3.7–4.4 regression results) was used for alkalinity measurements (Finnish Standard SFS-EN ISO 9963-2).

Monthly flow-adjusted and non-flow adjusted TIC fluxes were calculated with the FLOWNORM 2.1 programme (Libiseller and Grimvall, 2002). The total TIC export from unmonitored catchments (9% of the total catchment area) was estimated by extrapolating export from nearby monitored catchments with similar land cover characteristics using an area specific export coefficient.

Trends in export and concentration were analysed with the seasonal Kendall test (Hirsch et al., 1982, 1991), using both non-adjusted as well as flow-adjusted values. The magnitude of statistically significant trends was estimated according to the seasonal Kendall slope estimator (Hirsch et al., 1982). Based on the graphical outputs we noticed that TOC concentrations commonly decreased from 1975 to the mid-1990s and started to increase after that. Therefore we divided the whole 40-year study period into two periods of equal length (1975 to 1994 and 1995 to 2014), and also analysed trends for these two periods.

3. Results

3.1. Concentrations of carbon

Median river specific TIC concentrations varied from 1.6 mg C L^{-1} to 12.0 mg C L^{-1} and the respective TOC concentrations were 5.7 mg C L^{-1} to 21.0 mg C L^{-1} (Table 1). The highest TIC concentrations were measured in rivers draining croplands, whereas the highest TOC values were found in peat dominated catchments, where TIC concentrations were low (< 3 mg C L^{-1}). The lowest TOC concentrations were found in catchments in northernmost Finland and in catchments with the highest percentage cover of lakes (Fig. 3). These effects of land type characteristics were also seen in TIC:TOC concentration ratios, which varied from 0.07 to 1.12 (Table 1).

The highest TIC concentrations were measured during the low-flow periods in February and March and the lowest concentrations during the high flow periods in May. This is quite the opposite from that of TOC, which had low concentrations in February and March, and then the concentrations increased during the snow-thaw period of April to May. However, the highest seasonal TOC concentrations were measured in late summer or early autumn. TIC correlated negatively with flow in every river, whereas TOC had positive correlation with flow in most of the rivers (Table 1). In catchments with numerous lakes the TOC-flow correlation was weaker.

Table 1. Basic TOC, alkalinity and TIC statistics and runoff in 29 Finnish rivers.

3.2. Export of carbon

During the whole study period on average Finnish rivers exported annually 260,000 t TIC into the Baltic Sea and the annual TOC export was 918,000 t. Therefore Finnish rivers exported annually nearly 1.2 Mt carbon to the Baltic Sea, and 80% of the TC export was in the organic form (Fig. 2). In addition, the largest Finnish river basin, the Vuoksi River (Basin No. 4) discharged 52,000 t of TIC and 140,000 t of TOC per year into Lake Ladoga located in Russia that is also part of the Baltic Sea catchment area. Inter-annual variations in TC export ~~was~~ high (0.6 to 1.7 Mt C yr^{-1}) which was mostly dependent on the hydrological conditions. During wet years (e.g. 2008) the proportion of TOC export increased in comparison to TIC export. To smooth out the inter-annual differences in riverine carbon export caused by hydrological patterns we calculated five-year ~~mean~~ export values. The highest water flow and TC export occurred between 1980 and 1984, which mainly resulted from high TOC exports. Water flow was at its lowest from 1975 to 1979 resulting in a low TC export (Fig. 2). From 2005 to 2014 TIC export was at its highest, and the mild winters also increased TOC export leading to high TC export. TIC:TOC export ratios were usually lower than TIC:TOC concentration ratios (Tables 1 and 2).

Table 2. TOC, TIC and TC export of 29 Finnish rivers.

The highest area specific TOC export (8.0 g C m^{-2} yr^{-1}) was measured in a small river basin with no lakes, some croplands and high (>20% of the catchment) peatland area (Fig. 3 and Table 2). The highest area specific TIC export (>2.0 g C m^{-2} yr^{-1}) was found in rivers located in south-western Finland's heavily cultivated catchments (Fig. 4), whereas in peat dominated catchments the area specific TIC export was commonly below 1.0 g m^{-2} yr^{-1}. Three catchment characteristics, lakes, peatlands and croplands, had the strongest impact on riverine TIC and TOC export: Lakes are efficient in retaining TOC (where retention includes both sedimentation and losses to the ~~atmosphere)~~ whereas they seemed not to have a strong influence on TIC export (Fig. 5a). Peatlands are the major source of TOC in Finnish watercourses and they have a negative impact on TIC export (Fig. 5b). Croplands contribute greatly to TIC export, but not so much to TOC export (Fig. 5c).

3.3. Trends of carbon

3.3.1. Trends of carbon concentrations

No statistically significant ~~changes were measured~~ in river flow except in the two northern rivers (the Simojoki, Basin No. 64; and Tornionjoki rivers, Basin No. 67) in which the annual river flow increased between 1975 and 2014. During the whole 40 year study period 12 positive trends were detected in TOC concentrations, whereas two rivers, formerly heavily polluted by pulp and paper industry, had a negative trend. TOC concentrations decreased in 19 of the 29 rivers from 1975 to 1994 and the median magnitude of the decrease was 30% (Table 3). An upward trend in TOC concentration was discernable in 21 rivers from 1995 to 2014 and the median magnitude of this increase was 26%. The changes (both decreases and increases) during the two periods were detected in different parts of Finland and in rivers with different catchment properties.

Between 1975 and 2014 TIC concentrations increased in 19 rivers and decreased in one river and the median magnitude of the increase was 37%. In contrast to TOC concentrations, the TIC concentrations showed a more uniform trend during the 40 year period: They increased in Southern Finland and did not change in Northern Finland (Table 4). There were differences in TIC concentrations between the periods investigated: From 1995 to 2014 increases were more common than during the two previous decades, and decreases were detected in three rivers in Northern Finland (the Oulujoki, Basin No. 59; Kiiminginjoki, Basin No. 61, and Simojoki rivers, Basin No. 64).

Table 3. Trends, significance, slope and proportional change of TOC concentrations in Finnish rivers from 1975 to 2014, 1975 to 1994 and 1995 to 2014.

Table 4. Trends, significance, slope and proportional change of TIC concentrations in Finnish rivers from 1975 to 2014, 1975 to 1994 and 1995 to 2014.

3.3.2. Trends of carbon export

The overall trend in TC export was positive since the early 1990s and both TOC and TIC export increased to contribute to this trend (Fig. 2). There were differences in the trends of the region~~-wise~~ export: Rivers in the Gulf of Finland and the Bothnian Bay drainage basin showed the most evident positive trend in TOC export, whereas export to the Bothnian Sea and Archipelago Sea dropped during the last five-year period mainly due to decreased flow (Fig. 3). TIC export increased to all sub-regions of the Baltic Sea, except into the Bothnian Bay. The most remarkable increase has been into the Gulf of Finland (Fig. 4), where the upward trend was quite linear until the end of our study period irrespective of the changes in water flow.

Compared to the trends in TOC concentrations the river-~~wise~~ trends in TOC export were less statistically significant, and the magnitude of the change was ~~of~~ relative minor ~~importance~~ (<3%) over the 40 year period (Table 5). From 1975 to 1994 only one statistically significant (negative) trend could be deduced, whereas from 1995 to 2014 TOC export increased in five rivers, four of them situated in Northern Finland.

Trends in TIC export and concentrations were more similar in terms of the number of rivers with statistically significant trends than the respective TOC results. TIC export increased from 1975 to 2014 in 12 rivers and decreased in one (Table 6), and the magnitude of the changes differed remarkably: The proportional increase in TIC concentrations was 37% and the respective TIC export increase 3%. Flow normalisation removed the upward TIC and TOC trends in the Simojoki River (Basin No. 64, northern Finland) and thus the increasing TC export could be attributed to the increased water flow during winter.

Table 5. Trends, significance, slope and proportional change of TOC export of Finnish rivers from 1975 to 2014, 1975 to 1994 and 1995 to 2014.

Table 6. Trends, significance, slope and proportional change of TIC export of Finnish rivers from 1975 to 2014, 1975 to 1994 and 1995 to 2014.

3.3.3. Seasonal trends

Despite being able to detect only few rivers with annual changes in flow, the seasonality of the flow changed over the study period: Flow decreased in nearly half of the rivers ~~in May~~ between 1975 and 2014 (Fig. 6a). These rivers were mainly located in southern Finland. In contrast the winter flow rates increased in northern Finland. There were no overall changes in flow between 1975 and 1995 (Fig. 6b) and the decrease in flow in May occurred between 1995 and 2014 (Fig. 6c).

Monthly TOC concentrations showed proportionally more increases than decreases between 1975 and 2014 (Fig. 6a). The increases were common during the winter and decreases during the summer. Clear ~~periodical~~ differences were observed in TOC trends: Only decreases were detected between 1975 and 1995 (Fig. 6b), whereas only increases were recorded between 1995 and 2014 (Fig. 6c). Fewer rivers showed increases in the monthly export compared to the concentrations over the whole period and the most remarkable difference was the decrease in export in May (Fig. 6a). The clear differences in the trends of TOC concentrations between the two periods (1975 to 1994 vs. 1995 to 2014) were not clearly reflected in the ~~periodical~~ export trends (Fig. 6b and Fig. 6c).

TIC concentrations increased ~~commonly~~ in every month from 1975 to 2014 (Fig. 6d). From 1975 to 1994 few changes were detected except increases in May (Fig. 6e), which continued from 1995 to 2014 and upward trends were also detected in June in many rivers (Fig. 6f). TIC export was increasing in the winter months during the whole 40 years period (Fig. 6d). The ~~periodical~~ export trends showed few changes (Fig. 6e and Fig. 6f).

4. Discussion

4.1 Export of carbon

Peatlands cover one third of the Finnish land area and they have a strong influence on carbon dynamics of the Finnish freshwaters. TOC concentrations in rivers draining peat dominated-catchments are commonly close to 20 mg L^{-1}, whereas the respective TIC concentrations are below 1.0 mg L^{-1}. The influence of the high percentage of peat in Finnish catchments was clearly reflected in the riverine carbon export measured during this study period: TOC dominated and only 20% of the 1.2 Mt TC yr^{-1} export was in the inorganic form, which is similar to the respective proportion 75% of TOC in Norway (de Wit et al., 2015). This is opposite to the rivers in the contiguous USA, where over 75% of the carbon export is in inorganic form (Stets and Striegl, 2012) and also in North American Arctic rivers DIC is the predominant form in which carbon is exported to the coastal waters (Guo et al., 2012; Tank et al., 2012). The median TIC:TOC concentration ratio in the Finnish rivers was 0.54, which is considerably less than the ~~average~~ global ratio 1.9 (Meybeck, 1987; Tank et al., 2012).

Most of the inorganic carbon in rivers entering the Baltic Sea consists of bicarbonates (Kulinski and Pempkowiak, 2012), which originate~~s~~ from weathering of aluminosilicate or carbonate rocks. Silicate weathering dominates in Finland (Starr et al. 1998) as well as elsewhere in the boreal region (Millot et al., 2003; Zakharova et al., 2007). Inorganic carbon may also be derived from the decomposition of dissolved and particulate organic matter (Brink et al., 2007; Guo et al., 2012). In two northern Swedish rivers, silicate weathering was estimated to be responsible for about 70% of the inorganic carbon export and the rest originated mainly from respiration of organic matter in soils (Brink et al., 2007).

The highest TIC concentrations, and area specific export, were measured in rivers in Southern Finland draining urban and agricultural areas. The area specific TC export by Finnish rivers was 4.5 g C m^{-2} yr^{-1}, which was higher than the respective export of 4.0 g C m^{-2} yr^{-1} in Norway (de Wit et al., 2015) but less than the corresponding export of 5.5 g C m^{-2} yr^{-1} in the USA (Stets and Striegl, 2012). Three key factors decrease the riverine TC export from Finnish rivers: Firstly, the scarcity of carbonate rocks substantially reduces weathering rates leading to low TIC leaching (Lahermo et al., 1996). Secondly, lakes in Finland are efficient in retaining terrestrial-derived TOC (if losses to the atmosphere are also counted). Mattsson et al. (2005) estimated that the average annual retention of TOC in lakes in Finnish river basins is approximately 15 g C m^{-2} yr^{-1} ~~lake area.~~ In the boreal zone in Sweden 30 to 80% of the TOC entering lakes was estimated to be retained (Algesten et al., 2004), and in another Swedish study comprising 53 rivers the respective estimate was 50% (Weyhenmeyer et al. 2012). The fraction of the DOC input that is lost internally through sedimentation or degradation increases with water retention time (del Giorgio and Peters, 1994). However, not all TOC mineralised in lakes is lost from TC balances since the mineralisation process also generates TIC (Brink et al., 2007) and photo-degradation of NOM potentially contributes to alkalinity and buffering capacity (Köhler et al. 2002). Thirdly, Finland is sparsely populated and urban areas cover just 3.3% of the total land area. In Britain, the highest DIC concentrations were measured in highly urbanized catchments and an urban land cover of greater than ~5% seemed to be critical threshold for land-cover to affect DIC (Baker et al., 2008). Only 11of the 29 rivers included in our study had an urban area larger than 5%. In addition, carbon loading originating from point sources in Finland, especially from pulp and paper production, has decreased remarkably during the last three decades (Räike et al., 2012).

4.2 Trends of carbon concentrations and export

Annual water flow increased in two rivers in northern Finland, but more important, in regard of C export, were the seasonal changes: Flow decreased in May in southern Finland and increased in winter in northern Finland. Between 1975 and 2014 both TOC and TIC concentrations generally increased, and partly in the same rivers, but the timing and location of the trends differed markedly: Upward trends in TIC concentrations were more uniform during the 40 years, whereas TOC concentrations at first decreased and then started to rise (Tables 3 and 4). Furthermore upward TIC trends from 1975 to 2014 were located predominantly in southern Finland, and the respective TOC trends in more northerly peat-dominated catchments. Common to both parameters was that the trends in concentrations were not reflected in export trends (Tables 3 and 6). This was especially true for TOC.

4.2.1 Trends of TOC concentrations and export

The overall eutrophication status of the Finnish freshwaters is decreasing (Räike et al., 2003), but the TOC concentrations have been increasing in headwater streams and lakes (Vuorenmaa et al., 2006; Sarkkola et al., 2009). Most of the TOC in boreal freshwater systems is allochtonous originating from catchments and therefore increasing concentrations in freshwaters indicate that more organic carbon of terrestrial origin is leached into lakes and rivers. Beside the amount of organic matter produced in terrestrial ecosystems and its decomposition, TOC export to the sea is dependent on leaching into the aquatic systems and processes affecting its transport to the sea.

TOC concentrations between 1975 and 1994 decreased comprehensively in Finland, and after that (1995 to 2014) they started to increase (Table 3). The negative trend can mostly be explained by decreased point-source pollution: Organic matter export into the Baltic Sea originating from point sources is now less than 20% of the total export, whereas in the late 1980s it was approximately 50% (Räike et al., 2012). The upward trend was so ubiquitous, both in time and space, and it was not possible to link the changes to any specific catchment characteristics or single driver. It is likely, as also noted by other studies, that instead of one driver, several drivers are interacting simultaneously (Lepistö et al., 2008; Sarkkola et al., 2009) and that geographically drivers may vary (Clark et al., 2010).

One possible explanation behind the TOC increase is the recovery from acidification, which has occurred in Northern European terrestrial and aquatic ecosystems (Arvola et al., 2010; Evans et al., 2006; Monteith et al., 2007; Vuorenmaa et al., 2006). The mechanism behind this assumption is that increases in mineral acid inputs are buffered by decreasing solubility of organic acid and inversely declining sulphur deposition reduces soil solution acidity and increases the solubility of organic acids (Krug and Frink, 1983). Evans et al. (2012) estimated that recovery from acidification alone could have led to soil solution DOC increases between 46 and 126% since 1978 in the UK. In contrast, the solubility of organic matter decreased in Swedish upland soils, as a result of the acidification recovery (Löfgren and Zetterberg, 2011). They emphasised the role of riparian zone as a source of organic carbon as an explanation for this apparent discrepancy. Many studies have not found any major effects of acidification to changes in DOC (Clair et al., 2008; Lepistö et al., 2008; Sarkkola et al., 2009; Worrall and Burt, 2007). The differences in response to acidic deposition have been suggested to be linked to base cation status, which governs the sensitivity of the DOC response to deposition between catchments (Monteith et al., 2007). Acidic deposition started to decrease in Finland ~~on~~ the latter part of the 1980s and continued to decrease substantially up to1993. Since then there has been no remarkable change~~s~~ (Vuorenmaa, 2004). Even if the increases in TOC concentrations and the decrease in acidic deposition did not take place simultaneously we cannot eliminate the role of deposition in the changes, especially considering that the role of thresholds and time-lags in large-scale biogeochemical processes such as these. Acidic deposition was greatest in southern and western parts of Finland (Vuorenmaa, 2004) and it is unlikely that it has been the driving factor in northern Finland.

Changes in aquatic DOC concentrations/export have often been associated ~~to~~ climate change, which can affect OC in multiple ways (Evans et al., 2006; Freeman et al., 2001; Sarkkola et al., 2009; Worrall et al., 2003). The annual mean temperature in Finland has increased by about 0.7 ºC since 1900 (Jylhä et al., 2004), and this has influenced also river waters: Temperature increased in most of the rivers (in 24 of 29) and this increase happened mainly from 1995 to 2014 (data not shown). This in turn may have led to enhanced mineralisation of organic matter in the aquatic ecosystems. Sarkkola et al. (2009) demonstrated that stream temperature is one of the key drivers explaining TOC concentration trends in Finnish streams.

Although inland waters cover only about 3% of the Earth's surface area (Downing et al., 2006) they have a significant role in the sequestration, transport and mineralization of organic carbon (Algesten et al., 2004; Cole et al., 2007; del Giorgio and Peters, 1993; Kortelainen et al., 2006; Tranvik et al., 2009). In Sweden 50% of the total organic carbon entering lakes was estimated to be retained (Weyhenmeyer et al., 2012). In Finnish lakes permanent C accumulation in sediments has shown to be minor compared to CO_2 fluxes ~~through~~ lakes to the atmosphere (Kortelainen et al., 2006). We detected upward TOC trends also in catchments with high lake percentage, even if the proportional magnitude of the increase was generally smaller compared to lake poor catchments. This indicates that lakes were only partly able to mineralise increased terrestrial loading. On the other hand, the seasonality of TOC export has changed especially in southern Finland and winter fluxes have increased. During winter organic matter mineralisation is slower and photo-oxidation processes are weaker (Miller and Moran, 1997; Reichstein et al., 2000).

In Finland seasonal changes in discharge ~~has~~ been regarded as the most evident impact of climate change, especially increase in winter runoff (Veijalainen, 2012). Since 2004 Finland has experienced several relatively mild winters where instead of snow, precipitation fell as rain leading to high runoff and DOC export during the winter months. In the northernmost Finnish rivers the winter North Atlantic Oscillation index (NAO) ~~was detected to predict rather well~~ the TOC export in March (Arvola et al., 2004). The decreased amount of snow on the ground decreased DOC export during the spring thaw. Earlier melting periods in winter and spring, reduced the role of the spring runoff peak, and higher temperature and precipitation in autumn increased the autumn export peak. Despite the decrease in spring DOC export the total annual export was higher during mild winters than the long term mean export (Räike et al., 2012; Mattsson et al., 2015).

4.2.2 Trends of TIC concentrations and export

As a product of TIC concentration and water flow TIC export was affected by changes in water flow, but it was not influenced as strongly as the TOC export. In contrast to TOC, TIC concentrations correlated negatively with flow, which has also been found in British and North American Arctic rivers (Baker et al., 2008; Tank et al., 2012). TIC concentrations were the highest during low flow periods and the lowest during spring thaw, leading to lower annual TIC export compared to TOC. The high concentrations during the low flow periods indicated the importance of groundwater as a TIC source (c.f. Humborg et al., 2010; de Wit et al., 2015).

TIC export from Finnish rivers to the Baltic Sea increased from 1975 to 2014. It started to rise in the early 1990s and has been increasing nearly linearly since then. There are some clear regional differences: Rivers draining the agricultural-dominated Archipelago Sea catchment did not show change. Our results are partly contradictory to Hjalmarsson et al. (2008) who found that the alkalinity of rivers entering the Gulf of Finland was increasing and alkalinity in rivers entering the Gulf of Bothnia decreasing. One explanation for this difference could be the different time periods in these studies i.e. the time period in Hjalmarsson et al. (2008) was 100 years (1900–2000).

There are several driving factors, which may be behind the shifts in riverine TIC export. These include changes in weathering, acid deposition, leaching, land use and groundwater discharges (Millot et al., 2003; Raymond and Cole, 2003; Humborg et al., 2010). The positive trend in alkalinity in the ~~River~~ Mississippi, and also in many other North American rivers, has been linked to changes in agricultural practices (Raymond and Cole, 2003; Stets et al., 2014). However, we could not find an overall increasing trend in the rivers draining most heavily cultivated areas in Finland. Furthermore, during the last decades there have been no significant changes in the land use. Few increases in Mg concentrations (data not shown) did not indicate that the amount of groundwater in river flow has increased, which does not support the possibility that increases in TIC concentrations and export have been caused by increased TIC discharge from groundwater.

As stated earlier in Finland, sulphur deposition started to decrease in mid 1980s and the strongest decrease happened in southern Finland between 1987 and 1993 (Vuorenmaa, 2004), earlier than the riverine TIC export began to increase. Acid deposition has decreased and positive trends in alkalinity and pH since the early 1990s have been common in small headwater systems in Europe and North America indicating recovery from acidification (Stoddard et al., 1999). In a recent study of acid sensitive sites in North America and Europe alkalinity increased in 11 of 12 regions between 1990 and 2008, and also DOC concentrations increased (Garmo et al., 2014). Similarly, Hjalmarsson et al. (2008) linked the increasing alkalinity in Swedish rivers, beside changes in land use, to decreased acid deposition. In Swedish acid-sensitive lakes alkalinity has increased only slightly, whereas the increase in DOC concentration was remarkable (Futter et al., 2014).

We analysed TIC and TOC export trends for the whole 40 years period and detected that increases in TIC export were more common in rivers with high lake percentage in their catchment. As increases in TOC concentrations in Finnish freshwaters were first detected in upstream lakes and streams (Vuorenmaa et al. 2006; Sarkkola et al. 2009), but not at the river mouths TOC mineralisation in lakes might have contributed to those differences. TIC increase in the rivers might be linked to lake processes and water residence time. Lakes in the catchment increase water residence time enabling e.g. more efficient organic matter degradation (either in lake water, or sediments). Finnish lakes have been shown to decrease TOC transport to the sea (Mattsson et al., 2005; Räike et al., 2012) and to release significant amounts of CO_2 to the atmosphere (Rantakari and Kortelainen, 2005; Kortelainen et al., 2006), thus contributing to landscape biogeochemical processes linked to alkalinity production. Part of the increased TIC export to the sea could originate from mineralization of organic carbon (Brink et al., 2007). Dividing the 40 years study period into two parts revealed that the positive trend in TIC export did not coexist simultaneously with increase in TOC concentrations and therefore it is unlikely that mineralization would have been the major driver behind the increase.

4.2.3 Why are trends in TOC export and concentrations not similar?

Fewer upward trends in TOC export were recorded from 1975 to 2014 compared to trends in concentrations (Table 5) and the magnitude of the export increase was negligible (median increase in export was 1.7% vs 11% in concentrations). During the period 1995 to 2014 TOC concentrations increased in 21 rivers (median increase 26%) and export in 6 rivers (median increase was 5.9%). There is still a clear discrepancy between the export and concentration trends, but slightly increasing TOC export to the Finnish coastal waters is in agreement with increasing TOC concentrations in Finnish coastal waters in the 27 years from 1975 to 2011 (Fleming-Lehtinen et al., 2015).

The variation in TOC export followed closely changes in water flow, whereas the increase of TIC export was more independent of hydrological shifts: e.g. low water flow period between 2000 and 2004 did not stop the positive trend (Fig. 2). Changes in flow had ~~an overarching~~ influence on TOC export to the sea and the changes in concentrations were masked behind the variation in flow, which was noted also in a

Canadian study (Eimers et al., 2008). Normalising the data by flow reduced the variability (especially in small catchments) allowing the trends to be elucidated and nearly all rivers had an upward trend in normalised TOC export in southern Finland, although in general the magnitude of the changes were very slight (<4%).

It is evident that the increases in TOC concentration during the spring thaw in southern Finland were counterbalanced with decreases in flow and the amount of TOC exported to the sea in May decreased. This is important since the major share of annual TOC was ~~exported from 1975 to 1994 to the sea during the spring freshet.~~ During the last year's mild winters over half of the annual TOC export in southern Finland may have discharged to the sea during the winter months.

4.3 Projected changes in C export/concentration and consequences

Climate change is projected to increase precipitation and runoff especially in the northern parts of the Baltic Sea over the next century (Graham, 2004). Scenarios predict further warming, wetter winters and drier summers in Northern Europe (Settele et al., 2014). Snow cover will diminish or almost vanish in southern Finland, and its duration will become shorter (Heino et al., 2008). Changes in the seasonality of flow might cause large shifts in DOC export geographically in Finland, since DOC export is linked to seasonal differences and catchment characteristics (Ågren et al., 2007, Rantakari et al. 2010; Mattsson et al. 2015). In a typical boreal catchment (peat coverage10-20%) DOC has been suggested to originate predominantly from wetland sources during low flow conditions, whereas during high flow forested areas are the main source (Laudon et al., 2011). Projected mild winters with shorter soil frost and/or snow cover periods will enhance chemical weathering, mineralization and leaching of carbon into the watercourses (Rantakari et al., 2010; Räike et al., 2012), which may lead to increased export of both TIC and TOC to the Baltic Sea (HELCOM, 2009; Omstedt et al., 2012).

Fleming-Lehtinen et al. (2015) demonstrated increasing TOC concentrations in Finnish coastal waters from 1975 to 2011. In contrast, based on the few available data from the open-sea area of the Baltic Sea, no trend towards increase in DOC concentrations can be found from the 1970s to 2010 (Hoikkala et al., 2015). Brownification of coastal waters will have multiple effects on the ecosystems as light climate change unfavourable to phytoplankton and bacterial production increases (Berglund et al., 2007). Mineralisation of organic matter impairs oxygen conditions in bottom wa~~s~~ters, which in turn may lead to anoxia and release of phosphorus from sediments (Lehtoranta et al., 2009; Conley et al., 2011).

Conclusions

The carbon in rivers near the river mouths integrate C loading from a variety of sources and processes over large land areas. Consequently, it is often difficult to differentiate the influence of single driving factors in the drainage basin. Instead of a single driver several drivers are interacting simultaneously and geographically the major drivers may vary. The upward trend in TOC concentrations in Finnish rivers was so ubiquitous, both in time and space since the mid' 1990s, that it is tempting to link it to the climate change: River water temperature was increasing, mild winters have been more common during the last twenty years, seasonality of flow and precipitation is changing etc. In addition, the recovery from acidification was partly behind the increase in southern Finland. Increasing OC concentrations will create many challenges to the protection of Finnish freshwaters, and although we did not find any substantial increase in the carbon export to the Baltic Sea, carbon concentrations in Finnish coastal waters have been shown to have increased (Fleming-Lehtinen et. al., 2015). This carbon is mostly originating from terrestrial sources and will create new challenges to the protection of Baltic Sea coastal waters.

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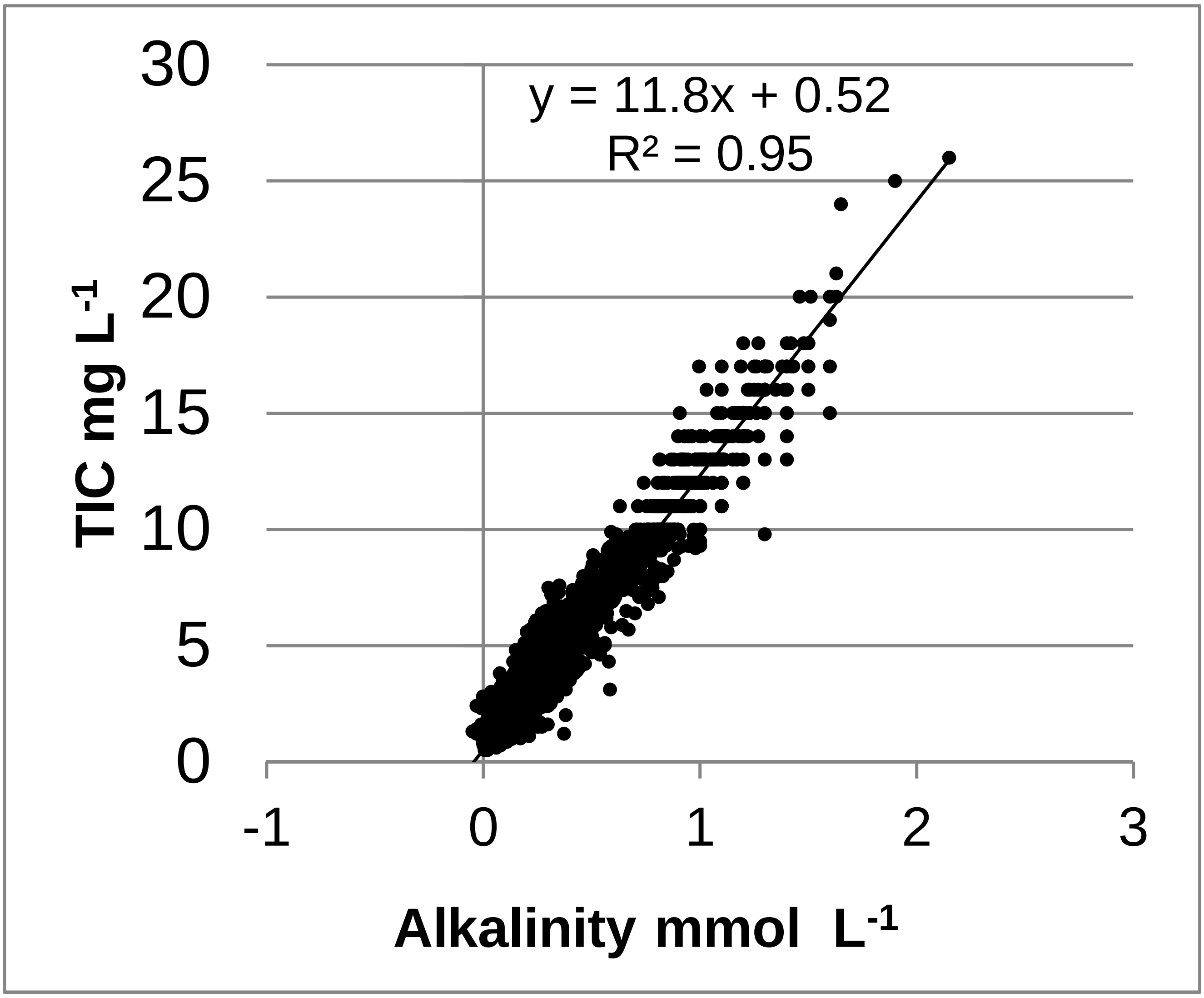
30
25
20
15
10
5
0
TIC mg L-1
y = 11.8x + 0.52
R² = 0.95
-1
0
1
2
3
Alkalinity mmol L-1

Figure
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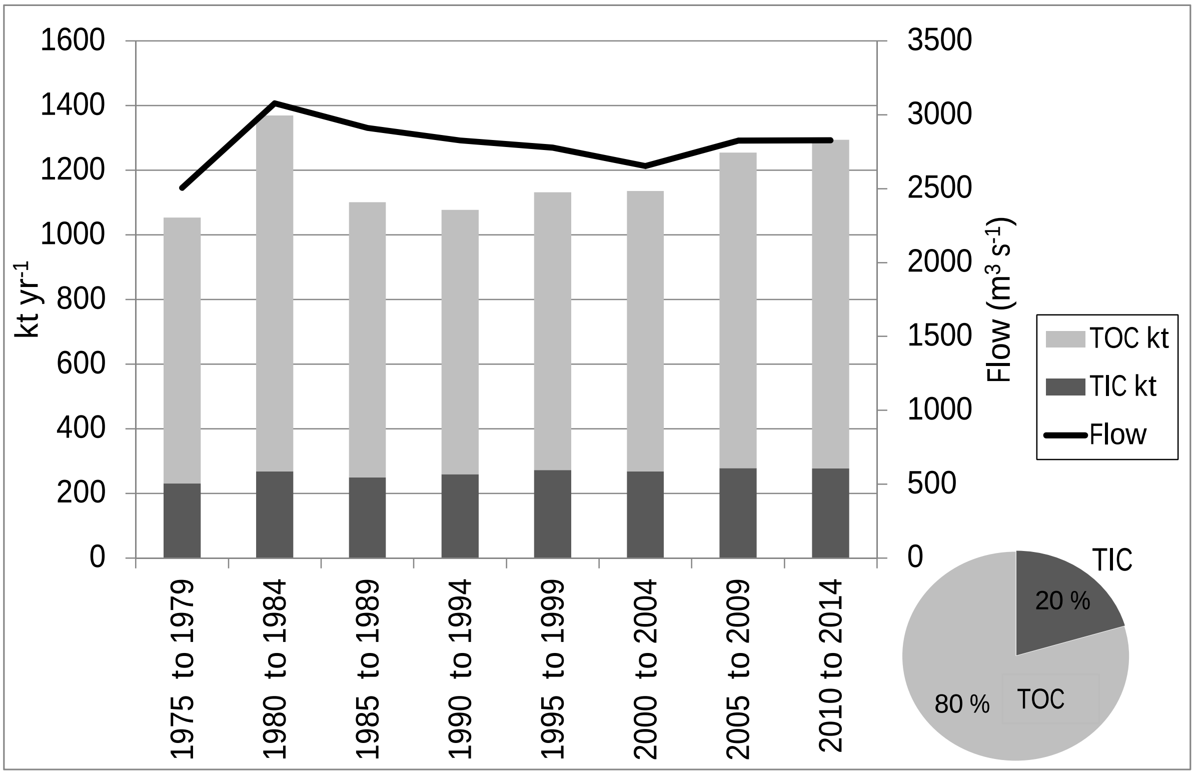

Figure
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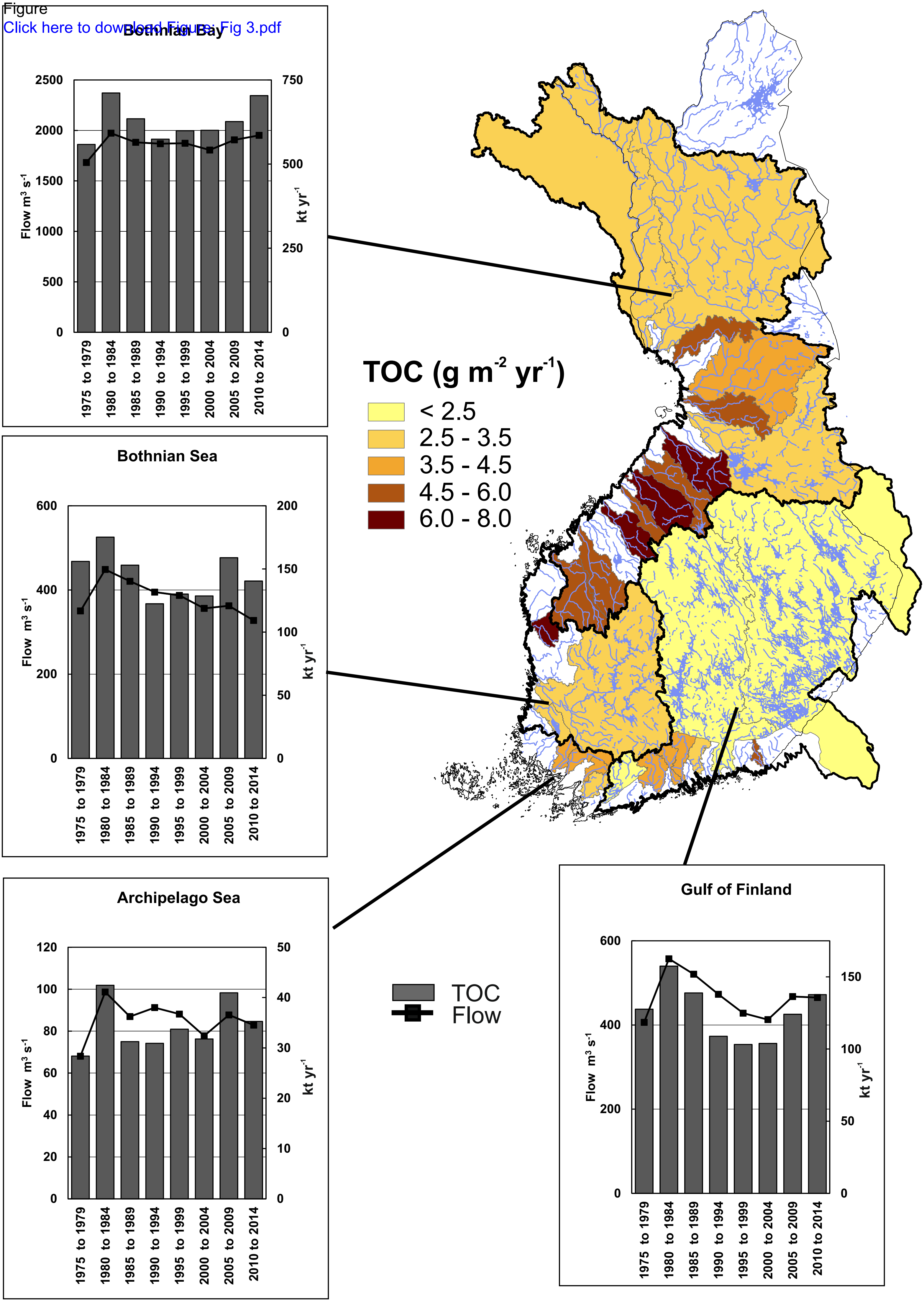

Figure
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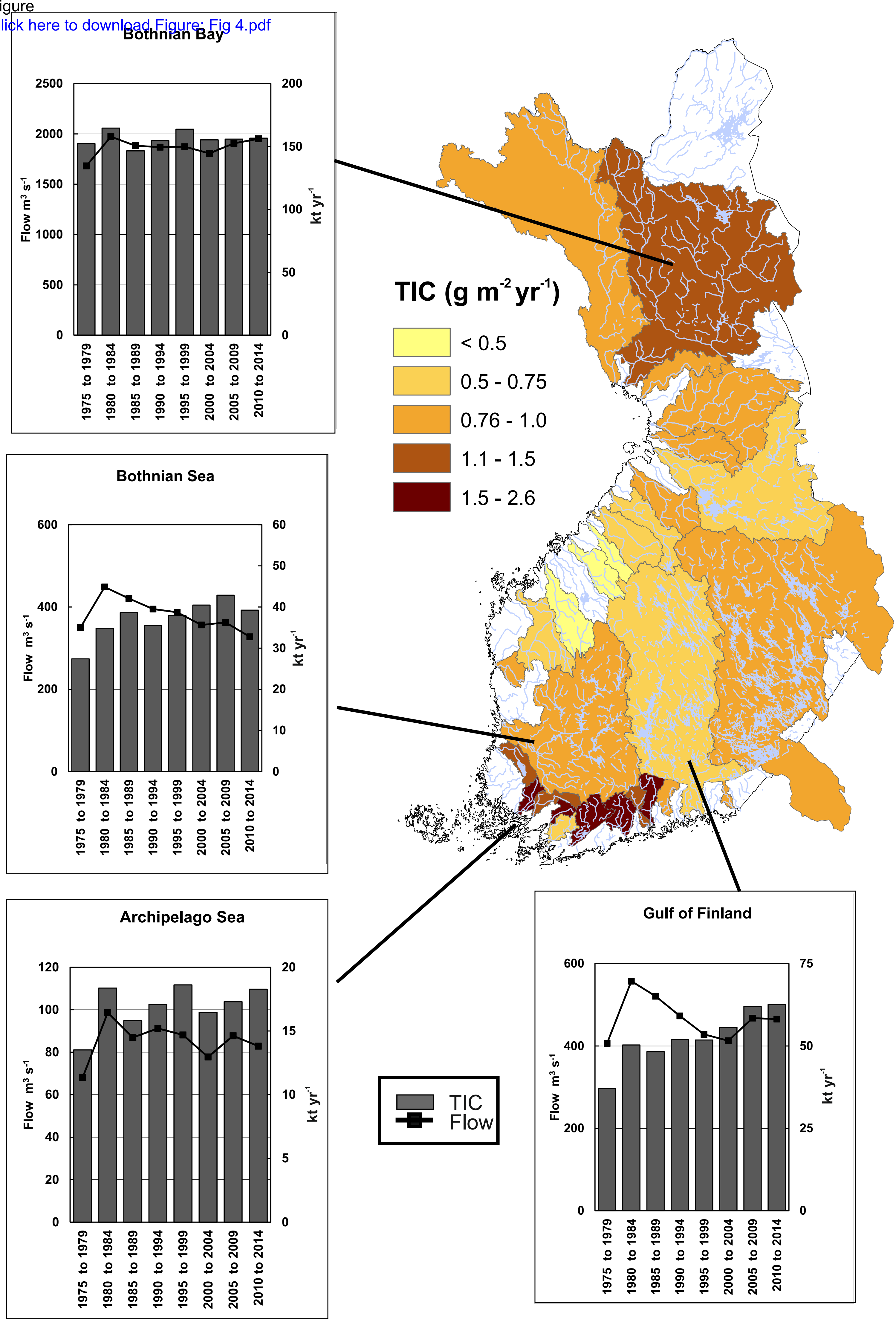
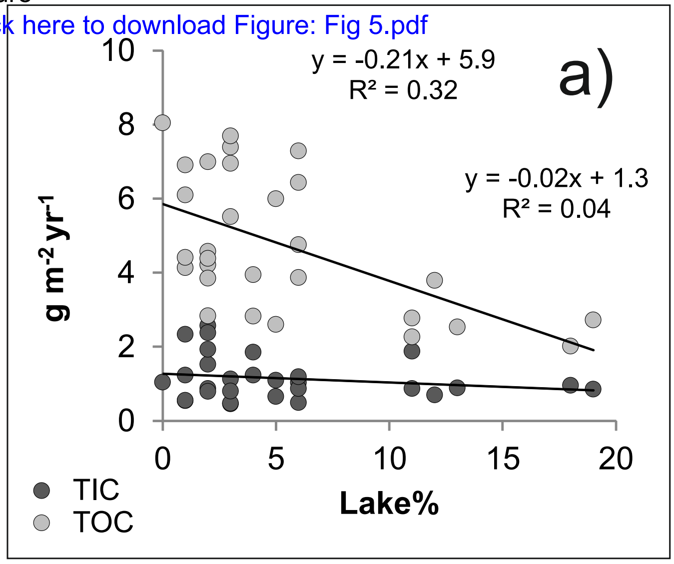
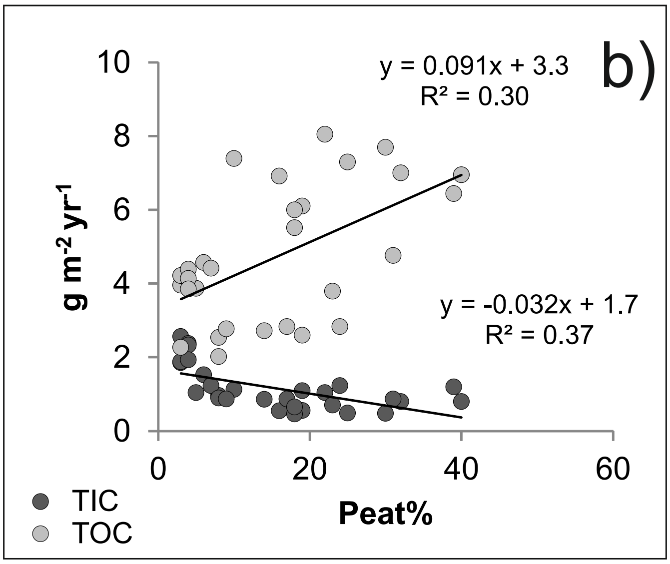
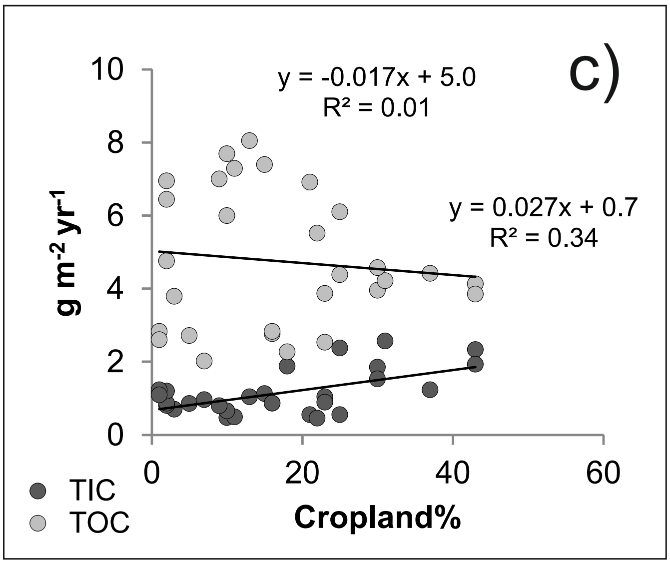
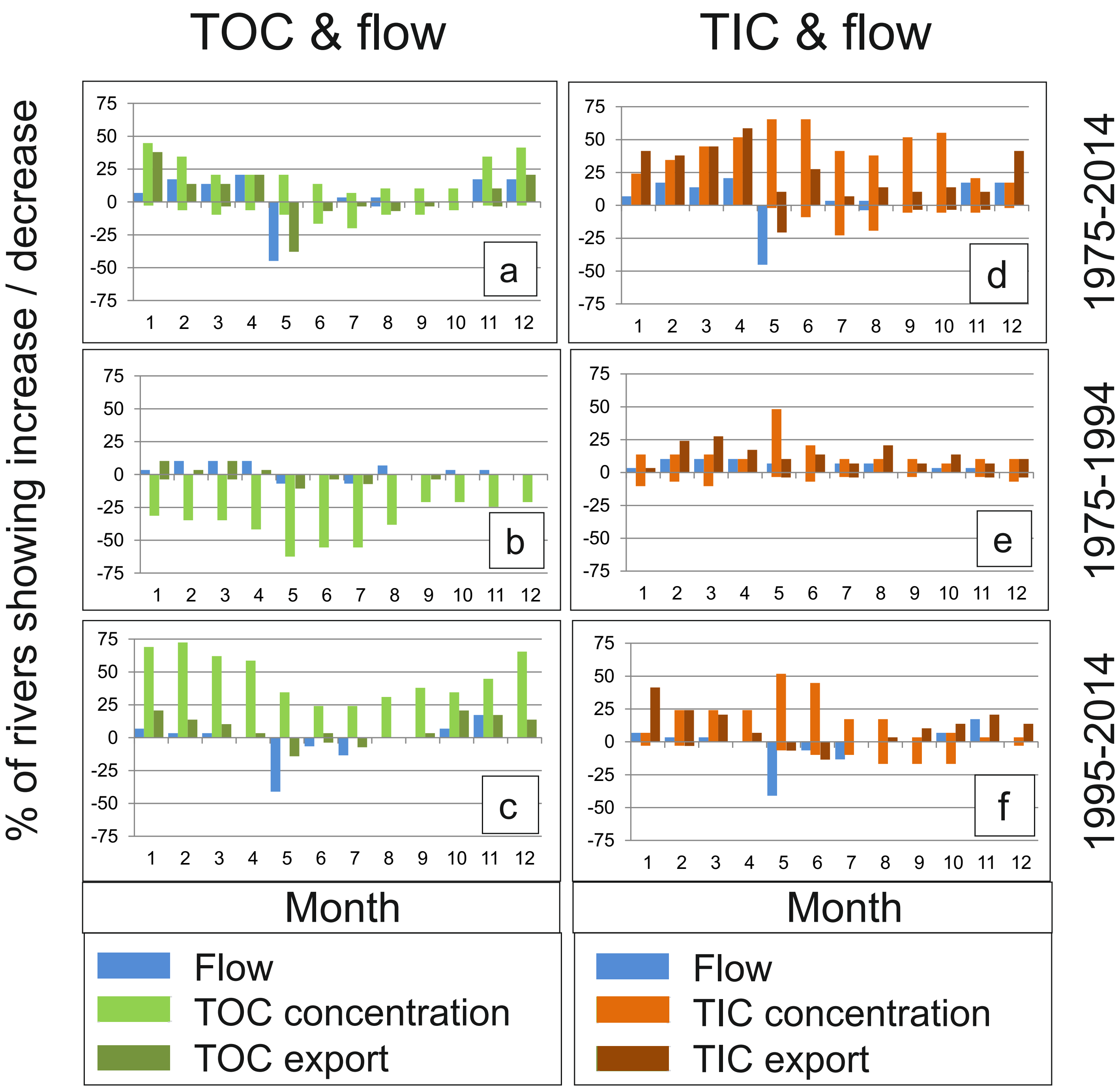



a)
y = -0.21x + 5.9
R² = 0.32
y = -0.02x + 1.3
R² = 0.04
g m-2 yr-1
Lake%
TIC
TOC


b)
y = 0.091x + 3.3
R² = 0.30
y = -0.032x + 1.7
R² = 0.37
g m-2 yr-1
Peat%
TIC
TOC


c)
y = -0.017x + 5.0
R² = 0.01
y = 0.027x + 0.7
R² = 0.34
g m-2 yr-1
Cropland%
TIC
TOC


TOC & flow
TIC & flow
% of rivers showing increase / decrease
1975-2014
1975-1994
1995-2014
a
b
c
d
e
f
Month
Month
Flow
TOC concentration
TOC export
Flow
TIC concentration
TIC export

Table
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Basin No	TOC analyses (n)	TIC analyses (n)	Alkalinity analyses (n)	Mean flow (mm)	TOC Median (mg l^{-1})	TIC Median (mg l^{-1})[1)]	TIC:TOC concentration ratio	TIC vs. alkalinity correlation	TIC vs. TOC correlation	TOC vs. flow correlation	TIC vs. flow correlation
4	477	46	566	377	7.0	2.7	0.36	0.67	0.10	-0.12	-0.62
11	280	134	269	394	15.0	2.9	0.16	0.90	-0.42	0.20	-0.32
14	706	149	688	271	7.8	3.5	0.44	0.76	-0.05	0.03	-0.65
16	367	153	381	305	9.8	7.6	0.65	0.93	-0.43	0.26	-0.59
18	461	154	509	295	11.0	11.0	0.82	0.98	-0.57	0.42	-0.66
19	362	153	375	263	14.0	7.5	0.49	0.97	-0.39	0.27	-0.56
21	502	153	502	292	12.0	10.0	0.79	0.96	-0.57	0.42	-0.66
23	441	152	455	255	7.9	7.7	0.90	0.95	0.41	-0.05	-0.43
24	362	87	383	322	10.0	4.4	0.40	0.94	-0.11	0.12	-0.40
25	393	104	390	308	11.0	12.0	1.12	0.96	-0.46	0.16	-0.55
27	422	93	450	261	12.0	9.4	0.70	0.96	-0.17	0.01	-0.53
28	421	97	533	263	14.0	9.1	0.56	0.98	-0.26	-0.05	-0.45
34	329	97	374	201	9.9	6.7	0.67	0.97	-0.39	0.61	-0.61
35	467	94	457	252	10.0	4.4	0.43	0.76	-0.22	0.56	-0.41
37	418	121	501	404	16.2	2.1	0.12	0.97	-0.77	0.34	-0.45
39	315	111	412	303	21.0	1.8	0.08	0.93	-0.16	0.15	-0.24
42	425	114	689	279	19.3	2.3	0.11	0.92	-0.08	0.04	-0.21
44	430	119	506	245	20.0	1.8	0.09	0.84	0.17	0.28	-0.22
49	398	117	512	303	20.0	1.6	0.07	0.83	-0.09	0.19	-0.16
51	384	117	570	299	20.0	1.7	0.07	0.92	-0.58	0.31	-0.30
53	420	156	611	353	21.0	2.7	0.11	0.85	-0.17	0.10	-0.25
54	500	189	550	287	18.0	2.5	0.13	0.90	-0.63	0.42	-0.32
57	480	189	614	313	19.0	2.4	0.12	0.78	-0.33	0.29	-0.21
59	519	168	524	372	9.4	1.9	0.18	0.48	-0.26	-0.09	-0.18
60	463	179	561	396	14.6	1.7	0.11	0.91	-0.51	0.25	-0.45
61	468	185	557	388	10.0	2.0	0.16	0.91	-0.66	0.57	-0.63
64	482	173	514	459	12.0	2.0	0.16	0.89	-0.54	0.40	-0.49
65	511	177	515	346	7.9	3.4	0.39	0.93	-0.64	0.55	-0.41
67	504	186	518	388	5.7	2.7	0.46	0.95	-0.48	0.48	-0.65
Median	430	149	512	303	12.0	2.7	0.36	0.92	-0.39	0.26	-0.45

Table
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Basin No	TOC export (t)	TIC export (t)	TC export (t)	TOC export (t km^{-2})	TIC export (t km^{-2})	TC export (t km^{-2})	TIC:TOC export ratio
4	143274	59437	202710	2.7	1.1	3.8	0.41
11	2641	378	3019	7.4	1.0	8.4	0.14
14	74862	34037	108899	2.0	0.9	2.9	0.46
16	3536	1850	5386	4.0	2.0	6.0	0.51
18	5365	3188	8552	4.2	2.6	6.8	0.61
19	3580	1214	4793	4.6	1.6	6.2	0.35
21	7389	4051	11440	4.4	2.4	6.8	0.56
23	4639	3947	8586	2.3	2.1	4.4	0.93
24	4052	1338	5390	3.9	1.3	5.1	0.33
25	2341	1612	3953	4.1	2.9	7.1	0.71
27	4192	2231	6423	3.9	2.1	6.0	0.55
28	3857	1504	5361	4.4	1.9	6.3	0.42
34	3387	1308	4695	2.5	1.0	3.5	0.39
35	74929	29363	104292	2.8	1.2	3.9	0.42
37	8831	965	9797	8.0	0.9	8.9	0.11
39	6856	547	7403	6.9	0.5	7.5	0.08
42	30044	2864	32908	6.1	0.6	6.7	0.09
44	22718	1838	24557	5.5	0.5	6.0	0.08
49	19406	1255	20661	7.7	0.5	8.2	0.07
51	10007	738	10745	7.3	0.5	7.8	0.07
53	12025	1532	13557	2.8	0.4	3.3	0.15
54	22253	2533	24786	6.0	0.7	6.7	0.11
57	30217	3454	33671	7.0	0.8	7.8	0.11
59	85353	16411	101764	3.8	0.7	4.5	0.19
60	26499	2940	29439	6.9	0.7	7.7	0.10
61	67487	12744	80231	4.8	0.9	5.6	0.19
64	20338	3277	23614	6.4	1.0	7.4	0.15
65	140020	60051	200071	2.8	1.2	4.1	0.44
67	90423	35782	126205	6.3	2.5	8.8	0.39

TOC concentration

Basin No.	1975 to 2014 Trend	p	Slope	Change %	1975 to 1994 Trend	p	Slope	Change %	1995 to 2014 Trend	p	Slope	Change %
4	↔	0.717	0.0		↘	0.001	-0.133	-38.1	↗	0.006	0.040	11.4
11	↗	0.000	0.1	17.1	↔	0.626	0.000		↗	0.004	0.177	22.1
14	↘	0.029	0.0	-12.0	↘	0.000	-0.200	-44.4	↗	0.000	0.093	24.8
16	↗	0.003	0.1	16.7	↘	0.003	-0.118	-26.3	↗	0.000	0.200	40.0
18	↔	0.059	0.0		↘	0.017	-0.080	-14.5	↗	0.011	0.167	30.3
19	↔	0.079	0.0		↔	0.302	-0.077		↔	0.056	0.125	
21	↔	0.884	0.0		↘	0.016	-0.129	-21.4	↔	0.183	0.056	
23	↗	0.001	0.1	21.4	↘	0.002	-0.231	-66.0	↗	0.000	0.146	36.0
24	↔	0.157	0.0		↘	0.011	-0.161	-33.6	↗	0.012	0.131	26.3
25	↔	0.541	0.0		↘	0.022	-0.167	-30.3	↔	0.077	0.089	
27	↔	0.139	0.0		↘	0.017	-0.135	-22.6	↔	0.103	0.068	
28	↔	0.078	0.1		↘	0.048	-0.192	-29.6	↗	0.026	0.125	17.9
34	↔	0.434	0.0		↘	0.005	-0.200	-40.0	↔	0.339	0.039	
35	↘	0.003	-0.1	-19.3	↘	0.000	-0.460	-76.7	↗	0.005	0.080	16.3
37	↗	0.003	0.1	13.2	↔	0.826	-0.007		↔	0.231	0.100	
39	↔	0.195	0.0		↘	0.026	-0.320	-30.8	↗	0.016	0.227	21.6
42	↔	0.061	0.1		↘	0.004	-0.180	-19.0	↗	0.004	0.250	25.0
44	↗	0.009	0.1	9.1	↔	0.824	-0.003		↗	0.005	0.272	27.2
49	↗	0.001	0.1	11.2	↔	0.645	-0.017		↗	0.005	0.286	28.6
51	↗	0.001	0.1	11.1	↔	0.392	-0.050		↗	0.009	0.250	23.8
53	↗	0.011	0.1	9.2	↔	0.373	-0.070		↗	0.002	0.333	31.7
54	↗	0.040	0.1	6.7	↔	0.113	-0.100		↗	0.010	0.250	27.8
57	↗	0.001	0.1	10.5	↔	0.075	-0.075		↗	0.002	0.286	28.6
59	↔	0.118	0.0		↘	0.005	-0.093	-20.7	↗	0.000	0.147	30.6
60	↗	0.000	0.1	13.7	↔	0.147	-0.084		↗	0.000	0.250	33.3
61	↗	0.009	0.0	8.7	↘	0.034	-0.082	-17.7	↗	0.002	0.143	26.0
64	↔	0.075	0.0		↘	0.049	-0.120	-21.9	↗	0.043	0.113	18.8
65	↔	0.094	0.0		↘	0.003	-0.130	-32.5	↔	0.514	0.015	
67	↔	0.167	0.0		↘	0.001	-0.150	-50.0	↔	0.971	0.000	

	1975-2014	1975-1994	1995-2014
↗	12	0	21
↔	15	10	8
↘	2	19	0
	29	29	29

↗	=	Increase
↔	=	No trend
↘	=	Decrease

Table
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TIC concentration

Basin No.	1975 to 2014 Trend	p	Slope	Change %	1975 to 1994 Trend	p	Slope	Change %	1995 to 2014 Trend	p	Slope	Change %
4	↗	0.000	0.025	34.4	↗	0.012	0.019	16.0	↗	0.026	0.014	9.3
11	↗	0.000	0.029	43.0	↔	0.807	0.000		↗	0.033	0.033	23.8
14	↗	0.000	0.052	59.8	↗	0.000	0.055	47.0	↔	0.709	0.002	
16	↗	0.000	0.042	24.5	↔	0.833	0.000		↔	0.111	0.041	
18	↗	0.000	0.077	36.3	↔	0.104	-0.063		↔	0.055	0.101	
19	↗	0.000	0.059	36.8	↔	0.966	0.000		↗	0.003	0.099	29.5
21	↗	0.000	0.078	38.8	↔	0.630	0.016		↗	0.001	0.160	35.8
23	↗	0.000	0.088	55.8	↔	0.125	0.024		↗	0.000	0.093	25.9
24	↗	0.000	0.035	35.9	↔	0.408	0.015		↔	0.110	0.029	
25	↗	0.000	0.096	35.9	↔	0.786	0.023		↗	0.003	0.149	27.1
27	↗	0.000	0.063	32.1	↔	0.927	0.000		↗	0.020	0.090	21.7
28	↗	0.008	0.044	24.3	↔	0.751	0.029		↔	0.054	0.071	
34	↗	0.000	0.105	80.9	↗	0.012	0.059	28.8	↗	0.006	0.102	35.9
35	↗	0.000	0.054	58.1	↗	0.000	0.052	33.2	↔	0.093	0.023	
37	↔	0.905	0.000		↔	0.891	0.000		↔	0.744	0.006	
39	↗	0.003	0.024	58.2	↔	0.485	0.000		↗	0.012	0.062	73.3
42	↗	0.002	0.023	49.1	↔	0.442	0.005		↗	0.005	0.063	73.2
44	↗	0.001	0.022	58.3	↔	0.135	0.020		↗	0.004	0.052	69.7
49	↗	0.006	0.009	26.9	↔	0.617	0.000		↔	0.090	0.016	
51	↔	0.091	0.005		↔	0.757	0.000		↔	0.184	-0.012	
53	↔	0.531	-0.003		↔	0.098	-0.026		↔	0.765	-0.004	
54	↔	0.230	-0.007		↔	0.918	0.000		↔	0.216	-0.025	
57	↗	0.030	0.010	16.7	↔	0.963	0.000		↔	0.089	0.026	
59	↔	0.987	0.000		↗	0.016	0.007	6.4	↘	0.003	-0.020	-19.3
60	↘	0.011	-0.012	-22.8	↔	0.354	-0.009		↘	0.010	-0.038	-38.3
61	↔	0.472	-0.001		↔	0.974	0.000		↔	0.330	-0.010	
64	↔	0.249	-0.005		↔	0.627	0.005		↘	0.016	-0.032	-25.0
65	↔	0.397	0.003		↔	0.969	0.000		↔	0.343	-0.014	
67	↔	0.990	0.000		↔	0.224	0.009		↔	0.289	-0.013	

	1975-2014	1975-1994	1995-2014
↗	19	5	11
↔	9	24	15
↘	1	0	3
	29	29	29

↗	=	Increase
↔	=	No trend
↘	=	Decrease

TOC export

Basin No.	1975 to 2014 Trend	p	Slope	Change %	1975 to 1994 Trend	p	Slope	Change %	1995 to 2014 Trend	p	Slope	Change %
4	↔	0.303	-36.0		↔	0.770	-31.0		↔	0.172	155.4	
11	↔	0.294	0.4		↔	0.881	-0.2		↔	0.379	0.8	
14	↘	0.047	-47.9	-2.7	↔	0.205	-75.6		↗	0.027	162.8	6.4
16	↔	0.091	1.2		↔	0.928	-0.2		↔	0.089	5.3	
18	↔	0.640	-0.5		↔	0.771	-0.6		↔	0.372	3.7	
19	↔	0.891	-0.1		↔	0.814	-0.5		↔	0.512	-1.9	
21	↔	0.707	-0.5		↔	0.515	-2.0		↔	0.410	5.6	
23	↔	0.236	-1.9		↘	0.033	-10.4	-8.9	↔	0.375	3.9	
24	↔	0.724	0.3		↔	0.975	-0.1		↔	0.541	1.7	
25	↔	0.496	-0.2		↔	0.412	0.9		↔	0.349	-1.9	
27	↔	0.360	0.6		↔	0.854	0.4		↔	0.842	0.8	
28	↔	0.734	-0.2		↔	0.855	0.2		↔	0.311	-2.6	
34	↔	0.435	0.6		↔	0.286	2.6		↔	0.844	-1.0	
35	↘	0.013	-53.2	-2.7	↔	0.118	-86.3		↔	0.845	-13.1	
37	↔	0.570	0.7		↔	0.893	-0.4		↔	1.000	0.1	
39	↔	0.980	0.0		↔	0.172	-4.7		↔	0.489	2.3	
42	↔	0.325	5.2		↔	0.942	1.6		↔	0.082	30.6	
44	↔	0.082	8.3		↔	0.114	18.5		↔	0.074	24.6	
49	↗	0.037	8.5	2.1	↔	0.668	2.3		↔	0.070	26.9	
51	↗	0.049	3.3	1.7	↔	0.518	3.1		↔	0.057	12.3	
53	↗	0.022	12.2	1.7	↔	0.619	-5.2		↗	0.026	49.7	5.9
54	↔	0.567	1.9		↔	0.883	1.1		↔	0.075	28.1	
57	↔	0.113	9.0		↔	0.411	10.5		↗	0.020	54.9	8.0
59	↔	0.239	24.2		↔	0.698	-23.4		↔	0.102	104.5	
60	↗	0.025	9.2	1.6	↔	0.813	2.0		↗	0.027	35.0	5.5
61	↗	0.031	24.1	1.6	↔	0.586	-16.3		↗	0.023	87.3	4.8
64	↗	0.003	9.0	2.1	↔	0.618	2.0		↔	0.243	13.4	
65	↔	0.364	-22.3		↔	0.073	-133.8		↔	0.663	33.3	
67	↔	0.621	4.4		↔	0.248	-30.4		↔	0.714	28.2	

	1975-2014	1975-1994	1995-2014
↗	6	1	5
↔	21	28	24
↘	2	0	0
	29	29	29

↗	=	Increase
↔	=	No trend
↘	=	Decrease

Table
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TIC export

Basin No.	1975 to 2014 Trend	p	Slope	Change %	1975 to 1994 Trend	p	Slope	Change %	1995 to 2014 Trend	p	Slope	Change %
4	↗	0.000	51.27	4.0	↗	0.006	72.84	6.3	↔	44.750	0.1	
11	↔	0.254	0.06		↔	0.616	-0.08		↔	0.109	0.4	
14	↗	0.000	42.84	6.1	↗	0.001	71.16	12.1	↔	35.616	0.1	
16	↗	0.038	0.78	2.0	↔	0.292	1.16		↔	1.598	0.1	
18	↔	0.476	0.42		↔	0.897	0.21		↔	1.804	0.2	
19	↔	0.699	0.08		↔	0.875	0.05		↔	-0.444	0.6	
21	↔	0.067	1.33		↔	0.794	0.49		↔	3.898	0.1	
23	↗	0.029	1.72	2.0	↔	0.149	3.57		↔	1.229	0.6	
24	↔	0.087	0.49		↔	0.178	1.16		↔	0.211	0.8	
25	↔	0.972	0.01		↔	0.050	1.36		↔	-0.450	0.6	
27	↔	0.167	0.70		↔	0.432	0.99		↔	0.897	0.6	
28	↔	0.725	0.11		↔	0.305	0.57		↔	-0.630	0.5	
34	↗	0.009	1.08	3.8	↗	0.036	2.10	8.1	↔	0.597	0.6	
35	↗	0.006	22.21	3.4	↗	0.015	49.49	7.8	↔	-5.680	0.8	
37	↘	0.024	-0.32	-1.3	↔	0.984	-0.02		↔	-0.151	0.6	
39	↔	0.055	0.20		↔	0.222	-0.43		↗	0.927	0.0	8
42	↗	0.001	1.93	3.7	↔	0.052	2.39		↗	6.512	0.0	12
44	↗	0.001	1.27	3.7	↗	0.002	2.07	7.0	↗	4.157	0.0	11
49	↗	0.006	0.76	3.1	↔	0.230	0.67		↗	1.954	0.0	8
51	↔	0.093	0.28		↔	0.256	0.43		↔	0.844	0.1	
53	↗	0.029	1.50	1.7	↔	0.570	-0.76		↔	5.186	0.1	
54	↔	0.937	-0.05		↔	0.362	1.48		↔	2.425	0.2	
57	↔	0.152	0.87		↔	0.455	1.28		↗	5.677	0.0	8
59	↔	0.570	1.99		↔	0.086	14.75		↔	-8.438	0.3	
60	↔	0.621	-0.29		↔	0.884	-0.26		↔	1.828	0.3	
61	↔	0.069	3.54		↔	0.904	-0.54		↔	9.319	0.1	
64	↗	0.003	2.15	2.9	↔	0.267	1.70		↔	0.041	1.0	
65	↗	0.008	22.36	1.5	↔	0.916	2.80		↔	8.424	0.8	
67	↔	0.051	8.50		↔	0.359	10.59		↔	4.905	0.6	

	1975-2014	1975-1994	1995-2014
↗	12	5	5
↔	16	24	24
↘	1	0	0
	29	29	29

↗	=	Increase
↔	=	No trend
↘	=	Decrease

Figure captions

Fig. 1. Correlation between alkalinity and TOC in 29 Finnish rivers.

Fig. 2. Total riverine carbon export (kt yr^{-1}): Total inorganic carbon (TIC) and total organic carbon (TOC; bars) and flow (m^3 s^{-1}, line) from Finland to the Baltic Sea from 1975 to 2014 grouped into five-year periods. The pie chart shows the proportions of TIC and TOC to the total carbon export.

Fig. 3. Area specific total organic carbon (TOC) export (g m^{-2} yr-1, map) from Finnish catchment areas, TOC export (kt yr^{-1}, bars) and flow (m^3 s^{-1}, lines) by sea-regions from 1975 to 2014 grouped into five-year periods. Note: The scale of the y-axes differs.

Fig. 4. Area specific total inorganic carbon (TIC) export (g m^{-2} yr^{-1}, map) from Finnish catchment areas, TIC export (kt yr^{-1}, bars) and flow (m^3 s^{-1}, lines) by sea-regions from 1975 to 2014 grouped into five-year periods. Note: The scale of the y-axes differs.

Fig 5. Relationship between area specific total organic carbon (TOC) and total inorganic carbon (TIC) export (g m^{-2} yr^{-1}) and proportional (%) lake area (a), peat area (b) and cropland area (c) of the 29 river catchments.

Fig 6. Proportion (%) of rivers with an increase (positive values) or decrease (negative values) in flow, TOC and TIC concentrations and export during three different time periods. Altogether data covered 29 Finnish rivers.